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GB 1403197

GB 1261764

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(54) METHOD OF PRODUCING A  
SOLDERABLE CONDUCTIVE  
LAYER ON A SUBSTRATE

(57) The invention is concerned with electronics and in particular with printed circuit board production. Printed circuit boards have been produced by forming on a substrate a layer of a polymer which contains conductive particles; however such boards are not readily soldered onto. According to this invention a solder-

able electrically conductive layer is formed on a substrate in, for example, the production of a printed circuit, by coating the substrate with a composition comprising a binder and electrically conductive particles and also soluble particulate material. The particulate material is concentrated in the free surface of the coating and is subsequently dissolved out from the surface to leave pores which are then metallised. The metallised surface is readily solderable.

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## SPECIFICATION

## METHOD OF PRODUCING A SOLDERABLE CONDUCTIVE LAYER ON A SUBSTRATE

This invention relates to a method of producing a solderable layer on a substrate, and is particularly but not exclusively concerned with such methods when used to produce printed circuit boards bearing patterned layers.

There are already known a number of processes for the production of printed circuits in which dispersions based on organic polymers and containing metal particles, preferably silver particles, are applied to a non-conducting substrate such as hard paper or aluminium oxide. The application is for example, by spraying, transfer or screen printing in particular patterns; the dispersions are fixed on the substrate by a subsequent heat treatment. Electrical arrangements (printed circuits) which contain as binding component polymers having good cross-linking and therefore good thermosetting properties, such as epoxides or polyphenols, are also distinguished by good strength of adhesion in relation to the metal particles dispersed in the polymer. However there is a problem with electrical arrangements produced in this manner relating to electrical contacting; such printed circuits are not generally solderable.

Another process for the production of printed circuits is already known to us in Germany in which there is employed as the substrate for the conductor pattern a heat-curable or a thermoplastic plastics material. This substrate comprises on its surface, or on those parts of the surface which are to be provided with conductive paths, a mixture consisting of an insulating material having copper oxide particles finely distributed therein. The particles are bonded in the insulating material by curing. To produce the printed circuit, copper oxide particles on the surface are reduced to copper by the action of for example sulphuric acid or phosphoric acid; thereafter, the surface is rinsed and introduced into an electroless metal deposition bath in which copper or another suitable metal is deposited on the surface. The proportion by weight of the copper oxide particles in the insulating material fluctuates between 0.25% and 80%. In this process if the copper oxide content is at the lower end of the range it is sometimes necessary for the surface to be subjected to a mechanical treatment by abrasion in order thus to expose the surface of the copper oxide particles to the acid. Without this additional pre-treatment, the deposition would in this case take a number of hours. The substrate, once it has been treated with the acid must be further processed without delay since there is a danger that the exposed metallic copper may be subject to atmospheric oxidation. In electrical arrangements produced in such a manner the electrical conductivity is determined exclusively by the layer thickness of the deposited metal, e.g. copper, coating. In order to obtain good

conductivity, the layer thickness must be relatively great. However, the building-up of a relatively thick copper layer from an electroless copper-coating bath is a time-intensive process even without the above mentioned additional mechanical pretreatment. A further disadvantage is that the strength of adhesion of the copper coating applied by electroless deposition generally decreases with the thickness of the layer deposited; this in turn results in a reduction in the reliability of a soldered joint made with the coating.

According to the present invention there is provided a method of producing a solderable electrically conductive layer on a substrate which comprises

(i) forming on the substrate a coating of a composition comprising a binder and electrically conductive particles and have having soluble particulate material adjacent its free surface; and  
(ii) removing the particulate material from the surface and metallising the surfaces of the pores thereby produced.

In a preferred embodiment the composition includes a flotation agent to concentrate the particulate material at the free surface. Such a flotation agent, which may be for example a non-ionic or anion-active wetting agent, is preferably present in up to 3% by weight, based on the weight of binder.

In a preferred embodiment the binder, which is preferably thermoplastic up to 175°C, is an organic polymer. It may be for example a system based upon a caprolactam-blocked addition product of isophorone diisocyanate and of an (hydr)oxyester containing a hydroxyl group. The organic polymer may alternatively be a mixture of caprolactam-blocked polyurethane with silicone resins and/or acetal resins and/or vinyl chloride-vinyl acetate copolymers. In this case the composition may be hardened by heating to a temperature whereat the polymer is crosslinked i.e. is cured, to give a hardened coating on which the remaining stages of the method are performed.

Preferably the composition also includes a reducing compound such as a sulphite salt.

The electrically conductive particles, by virtue of which the layer is conductive, are preferably silver particles, gold particles, nickel particles, particles of metals from the platinum metal group of the periodic table, silver-coated or gold-coated copper particles and/or mixtures thereof. The metal particles may be in platelet form or microcrystalline form, or a mixture thereof.

In order to vary the specific conductivity of the layer the ratio of the particles which confer electrical conductivity to the binder may be varied. The ratio by weight is preferably from 1:1 to 6:1.

The weight of soluble particulate material in the composition is preferably up to 30% of the weight of the conductive particles. The particulate material, which is preferably water soluble, may be for example a metal salt or a substance which forms a metal salt when treated with an acid.

Preferred metal salts are copper (II) sulphate, copper (I) chloride, copper (II) formate, copper (II) acetate, sodium chloride, sodium sulphide, lithium chloride, sodium carbonate, silver chloride, silver sulphate, silver nitrate and/or mixture thereof.

The composition, which may be coated on the substrate in the form of a paste, for example, may in particular be applied by spraying or printing, more particularly by screen printing.

There may be employed as the non-conducting substrate for example a hard paper, a temperature-resistant plastics material, a ceramic material or a metallic material with a non-conducting surface.

In addition, a substrate which is flexible may be employed.

The surfaces of the pores produced in the surface of the coating layer may be metallised in a galvanic metallisation bath; alternatively the metal layer may be autocatalytically deposited.

Preferably the surface is metallised with silver, copper or tin. In the case where the deposited metal layer consists of copper, it is preferably coated with a second, relative thin layer of a noble metal.

In a preferred embodiment the particulate material is soluble in the metallisation bath medium; thus the particulate material is removed to expose the surface pores and the metal layer is deposited in the pores in a single bath. In the case where the particulate material comprises a substance which forms a metal salt when treated with acid, it is of course necessary to carry out an acid pretreatment stage to convert the substance to metal salt before removal and deposition can take place. Preferably in this case the bath medium is itself acidic so that conversion, removal and deposition can all take place in the same bath.

It is not necessary in all cases to metallise the whole of the surface of the conductive coating. Indeed in certain circumstances it is much preferred that only certain parts of the coating are metallised to provide an area where other components may be soldered into the coating. In such cases the areas which are not to be metallised may be coated with for example a mask of a lacquer before treatment in the metallisation bath.

In a preferred embodiment of the invention, the composition is also applied to the inside surfaces of apertures which are provided in the substrate so as to form a contacting means passing through the substrate. The composition may be applied to the inside surfaces of the apertures, for example by sucking of the paste through the apertures by negative pressure.

In a further embodiment a coating of the composition is applied to both sides on a non-conducting substrate, the coatings being electrically connected by apertures in the substrate which are entirely or partially filled with the composition. Here again, those parts or areas of the coating which are not to be metallised may be masked by a solder-stopping lacquer.

In another embodiment more than one coating of composition is applied to the or each surface of

the substrate. The coatings are disposed one above the other in sandwich form in a number of planes separated by insulating layers, but are electrically connected by free zones in the insulating layer which contain conductive composition. The uppermost coating of this arrangement is metallised, where necessary after first applying a solder-stopping lacquer to parts of its surface.

A particularly preferred embodiment of the invention provides a method which comprises providing a curable electrically conductive composition comprising a curable organic polymer which has electrically conductive particles dispersed therein and which also contains particles of a metal salt and/or a substance which forms a metal salt when treated with acid, and a flotation agent which concentrates the salt and/or substance at the surface of a layer of the composition when the composition is cured. A coating of the composition is applied to a non-conductive substrate and is then cured to form a hardened layer of the composition having particles of salt and/or substance concentrated at its free surface. The particles of salt or salt formed from the substance are then dissolved from the surface of at least a part of the hardened layer to form surface pores therein, and the layer is treated in a galvanic or autocatalytic metallisation bath to deposit the bath metal in the pores and form a layer element at least a part of which has a solderable metallic surface layer.

The following Example illustrates the invention.

#### EXAMPLE

There was dispersed in a polyurethane-based binder which was blocked to crosslinking up to a temperature of 175°C, a mixture of silver particles in microcrystalline and platelet form, a proportion of a water-soluble copper salt, a proportion of a reducing sulphite compound, and a proportion of a non-ionic wetting agent. The paste thus obtained was pattern-wise impressed upon a hard paper substrate by means of screen printing to form an arrangement comprising the desired conductor paths or laminar patterns. The coating of composition was then cured by heating. During the curing of the binder, which was blocked against crosslinking up to 175°C, i.e. which was thermoplastic up to that temperature, the so-called flotation effect took place, the copper salt particles passing thereby to the free surface of the coating. This concentration of the individual metal salt particles at the surface of the binder had the result that when the workpiece was immersed in an electroless (autocatalytic) metallisation bath, these metal salt particles, which were of a size of about 5 µm, were dissolved out into the bath medium and left behind a large number of micro-cavities which were very close together and were distributed over the whole surface of the composition. The metallisation bath was a copper deposition bath, and the inside walls of the cavities were active in relation to the copper layer which was deposited from the bath, thus providing an initiator effect for the electroless metal deposition process.

The copper salt, in this case  $\text{CuSO}_4$ , dissolved out into the bath had no disturbing effect on the stability of the bath and facilitated the optimum control of the latter. The cavity-like pores formed when the copper salt was dissolved out optimised the anchoring of the copper layer which was built up from the cavities. It was observed that the presence of the reducing sulphite salt improved the conductivity of the workpiece obtained and accelerated the deposition of the copper from the bath.

The copper layer deposited on the hardened composition did not function primarily to provide the electrical conductivity of the conductor paths, but was necessary chiefly to provide a satisfactory solderability of the electrical arrangement. Since actual electrical conductivity of the conductor paths or laminar patterns was determined by the silver particles dispersed in the binder, the copper layer deposited from the metallisation bath could be made relatively thin; the initial phase of the deposition process during which the copper layer built up relatively rapidly was thus sufficient to provide a workpiece having good solderability.

Workpieces, for example printed circuits, produced by the method as exemplified above generally have good electrical conductivity and are at the same time solderable; further, the conductivity of the workpiece is not exclusively determined by the metal layer deposited from the metallisation bath. The anchoring of the metal layer to the coating on the substrate generally results in a high reliability of individual soldered joints made onto the workpiece.

The seeding point activation which is necessary in prior art methods is superseded in the method according to the invention by the removal of the particulate material, for example by an acid treatment with subsequent neutralisation and washing.

Since the electrical arrangement or circuit is already conductive in itself, the electrical circuit may be masked by a solder-stopping lacquer known *per se* before performing an electroless or optionally galvanic metallisation, in order to produce solderable contact points. Thus only the points at which the contacting is to take place are metallised and thereby rendered solderable. In this way, the quantity of metal necessary for the deposition from the catalytic or galvanic metallisation bath may be considerably reduced, thus facilitating satisfactory control of the bath permitting the method to be performed economically.

#### CLAIMS

1. A method of producing a solderable electrically conductive layer on a substrate which comprises

- (i) forming on the substrate a coating of a composition comprising a binder and electrically conductive particles and having soluble particulate material adjacent its free surface; and
- (ii) removing the particulate material from the surface and metallising the surfaces of the pores

thereby produced.

2. A method according to claim 1 wherein the composition includes a flotation agent to concentrate the particulate material at said free surface.

3. A method according to claim 2 wherein the composition contains up to 3% by weight of the flotation agent, based on the weight of binder.

4. A method according to claim 2 or 3 wherein the flotation agent is a non-ionic or anion-active wetting agent.

5. A method according to any one of the preceding claims wherein the weight of soluble particulate material is up to 30% of the weight of the conductive particles.

6. A method according to any one of the preceding claims wherein the particulate material comprises a metal salt.

7. A method according to any one of claims 1 to 5 wherein the particulate material comprises a substance which forms a metal salt when treated with an acid.

8. A method according to claim 6 or 7 wherein the metal salt is copper (II) sulphate and/or copper (I) chloride and/or copper (II) formate and/or copper (II) acetate and/or sodium chloride and/or sodium sulphide and/or lithium chloride and/or sodium carbonate and/or silver chloride and/or silver sulphate and/or silver nitrate.

9. A method according to any one of the preceding claims wherein the composition contains the conductive particles and the binder in a ratio by weight of 1:1 to 6:1.

10. A method according to any one of the preceding claims wherein the conductive particles are in the form of platelets and/or microcrystals.

11. A method according to any one of the preceding claims wherein the conductive particles are of silver and/or gold and/or nickel and/or silver-coated copper and/or gold-coated copper and/or a metal of the platinum sub group of the periodic table.

12. A method according to any one of the preceding claims wherein the binder is thermoplastic up to a temperature of  $175^\circ\text{C}$ .

13. A method according to any one of the preceding claims wherein the binder comprises an organic polymer.

14. A method according to claim 13 wherein the organic polymer comprises a mixture of a caprolactam-blocked polyurethane and a silicon resin and/or an acetal resin and/or a vinyl chloride-vinyl acetate copolymer.

15. A method according to claim 13 wherein the organic polymer comprises a caprolactam-blocked adduct of an isophorone diisocyanate and an oxyester containing a hydroxyl group.

16. A method according to any one of the preceding claims wherein the surfaces of the pores are metallised with silver, copper or tin.

17. A method according to claim 16 wherein the surfaces of the pores are metallised with copper and the metallic layer deposited in the pores is coated with a layer of a noble metal.

18. A method according to any one of the

preceding claims wherein the substrate is a hard paper, a temperature-resistant plastics material, a ceramic material or a metallic material having a non-conducting surface.

- 5 19. A method according to any one of claims 1 to 17 wherein the substrate is flexible.
20. A method according to any one of the preceding claims wherein the coating is formed on the substrate by spraying.
- 10 21. A method according to any one of claims 1 to 19 wherein the coating is formed on the substrate by printing.
22. A method according to claim 21 wherein the printing is screen printing.
- 15 23. A method according to any one of the preceding claims wherein only a part of the surface is metallised, the remaining part of the surface being masked with a lacquer to prevent metallisation.
- 20 24. A method according to any one of the preceding claims wherein the surfaces of the pores are metallised in a galvanic metallisation bath.
- 25 25. A method according to any one of claims 1 to 23 wherein the surfaces of the pores are metallised in an autocatalytic metallisation bath.
26. A method according to claim 24 or 25 wherein the particulate material is soluble in the metallisation bath, the removal of the particulate material and the metallisation of the surface pores thereby produced being performed in said bath.
- 30 27. A method according to claim 24, 25 or 26 when appendant to claim 7 or when appendant to any one of claims 8 to 23 which is itself appendant to claim 7, wherein the coating is treated with acid to convert the substance to the metal salt before the particulate material is removed from the surface.
- 35 28. A method according to claim 27 wherein the

metallisation bath is acidic and the substance is converted to the metal salt in the bath.

29. A method according to any one of the preceding claims wherein the substrate has an aperture and the composition is additionally applied to the aperture.
- 45 30. A method according to claim 29 wherein each surface of the substrate has a coating formed thereon, the two coatings being electrically connected by means of the composition applied to the aperture.
- 50 31. A method according to claim 29 or 30 wherein the composition is applied to the aperture by suction.
32. A method according to any one of the preceding claims wherein more than one coating of the composition is formed on the or each surface of the substrate, the electrically conductive coatings being separated by an insulating layer but electrically connected by composition which is present in free zones in the insulating layer, and the particulate material is removed from the uppermost coating.
- 60 33. A method according to any one of the preceding claims wherein the composition additionally includes a reducing compound.
- 65 34. A method according to claim 33 wherein the reducing compound is a sulphite.
35. A method according to claim 1 substantially as hereinbefore described.
36. A substrate having a solderable electrically conductive layer whenever produced by the method according to any one of the preceding claims.
- 70 37. A substrate according to claim 36 when in the form of a printed circuit board.
- 75 38. A device when comprising a printed circuit board according to claim 37.